

Localized Corrosion Studies on a Molecular Level

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Introduction

The corrosion resistance of technical passive alloys (e.g. stainless steels or aluminium alloys) is often limited by chemical or structural heterogeneities such as dislocations, grain boundaries, precipitates or inclusions. Inclusions play a key role in being potential nucleation sites for pitting and crevice corrosion. Many electrochemical methods to study localized corrosion processes are based on large-scale experiments with exposed areas in the $\text{mm}^2 - \text{cm}^2$ range. To understand the mechanisms of pit initiation and propagation it is useful to study the corrosion process in the micro- and nanometer range. During the past years various local electrochemical techniques have been developed which allow local surface measurements. Besides scanning techniques (1), where the immersed metal surface is scanned with a micro-reference electrode either in a static or vibrating mode, methods where only small areas are exposed to the electrolyte have also been proposed. These methods have the advantage that the current resolution can be drastically improved down to the pA - and even fA - range (2-5). Such microelectrochemical investigations provide often a better insight especially in the initiation mechanisms of localized corrosion (1-5).

Experimental Techniques

The microelectrodes used in these experiments basically consists of a microcapillary fixed like an objective to the revolving nose-piece of an optical micro-scope and filled with the appropriate electrolyte. The ground tip of the microcapillary can be varied from ~ 1 to $1000 \mu\text{m}$ in diameter. Additionally a sealing with a layer of silicon rubber is applied to prevent leaking of the electrolyte. This experimental technique not only allows an easy alignment of the microelectrode to the desired spot of the working electrode, it also limits the electrolytic contact to a small area to obtain current resolutions in the pA and fA range. Furthermore measurements can be performed on metal surfaces with a wide range of roughness (5,6). In order to perform electrochemical measurements in the micrometer scale several precautions were necessary. Besides good shielding to suppress electromagnetic interferences a specially modified battery operated high resolution potentiostat (Jaissle IMP 83 PC T-BC) with external impedance converter had to be used. Additionally, the remaining noise of the measured output signal was further reduced by a filter with lock in technique. Further details are given (5-7).

Furthermore incorporation of microsensors into the microcapillary cell enables to monitor additional chemical parameters such as pH values simultaneously with electrochemical measurements. This allows to gain important information especially with respect to non-stationary processes (8).

Results from Investigations of Stainless Steels

Recent investigations of localized corrosion processes on stainless steel showed, that the oxidizing dissolution of MnS-inclusions acts as pre-cursor process for pitting corrosion. Furthermore the size, the geometry as well as the presence of mechanical stress (9) are important

parameters for the transition of metastable to stable pitting. Microelectrochemical measurements using a capillary tip of $2.5 \mu\text{m}$ revealed that the interface inclusion/steel is the weakest zone of a MnS inclusion. The pitting of the interface is about 200 mV more negative than the one of the center of the MnS inclusion. Additional investigations with a modified microcell containing a pH sensor inside the microcapillary showed that metastable and stable pitting events acidified the local environment. The metastable pits decreased the pH of the electrolyte to values between 2 and 4. The stable pits caused the pH to decrease to ~ 2 (8).

Results from Investigations of Aluminum Alloys

The heterogeneous microstructure of many aluminum alloys have primarily been optimized for desirable mechanical properties, but such heterogeneities may render the alloys more susceptible to localized corrosion. In case of Al-2024-T3 alloy AlCuFeMn inclusions are more noble than the Al-matrix and act as cathode whereas AlCuMg inclusions are less noble than the Al-matrix and act as anodes (10-13).

The onset of pitting at single inclusions of the aluminum 2024-T3 alloy showed that the pit initiation process started only at a few AlCuMg inclusions within 200 mV of the pitting potential of large scale measurements (14). It was found that pit initiation occurs at the adjacent matrix of AlCuMg inclusions. Compared to AlCuMg inclusions the onset of pitting at AlCuFeMn inclusions took place at potentials 200 to 600 mV more positive. Microcracks in the bulk material, presumably formed by hydrogen evolution, were found to be the starting points for stable pitting. The onset of pitting at areas without inclusions occurred at potentials higher than $+500 \text{ mV}_{\text{SCE}}$. If copper was homogeneously dissolved in the matrix the resistance against pitting was strongly improved.

References

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